
BIOMATERIALS SCIENCE

An Introduction to Materials in Medicine

Edited by

Buddy D. Ratner and Allan S. Hoffman

*Center for Bioengineering and
Department of Chemical Engineering
University of Washington
Seattle, Washington*

Frederick J. Schoen

*Department of Pathology
Brigham and Women's Hospital
and Harvard Medical School
Boston, Massachusetts*

Jack E. Lemons

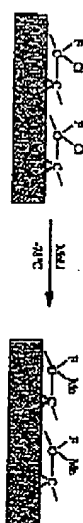
*Departments of Biomaterials and Surgery
School of Dentistry and Medicine
University of Alabama at Birmingham
Birmingham, Alabama*



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A Alkylation of poly(cis,cis,trans,trans)polybutadiene



B Trifluoroacetic anhydride reaction of a hydrogenated surface



C Glycidyl group introduction into a polyisocyanate

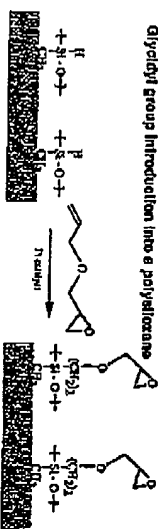


FIG. 2. Reaction of glycidyl groups in polyisocyanate (A), the trifluoroacetic anhydride reaction of a hydrogenated surface (B), and the glycidyl group introduction into a polyisocyanate (C). (A) (Mitsubishi Chemical, 1980), (B) (Chiba, 1980), (C) (Chiba, 1980).

nitrogen, carbon dioxide, or water vapor environments and the oxidation of metal surfaces in a mixture of alcohols. Specific chemical surface reaction changes only one functional group into another with a high yield and few side reactions. Examples of specific chemical surface modifications for polymers are presented in Fig. 2.

Radiation Grafting and Photografting

Radiation grafting and related methods have been widely used for the surface modification of biomaterials, and comparative reviews articles are available (Kramer, 1980; Hoffman et al., 1983; Stannett, 1980). Within this category, three types of reactions can be distinguished: grafting using ionizing radiation sources (from continuously, a cobalt-60 gamma radiation source), grafting using UV radiation (photografting) (Kramer and Brown, 1979; Denbick et al., 1991), and grafting using high-energy electron beams. In all cases, similar processes occur. The radiation breaks chemical bonds in the material to be grafted, forming free radicals, peroxides, or other reactive species. These reactive surface groups are then exposed to a

monomer. The monomer reacts with the free radicals at the surface and propagates in a free radical chain reaction, incorporating other monomers into a surface-grafted polymer.

Three distinct reaction modes can be distinguished: (1) In the unimodal (monomer 2, solvent) that is then exposed to the radiation source. (2) The substrate material can also be exposed to the radiation under an inert atmosphere or at low temperatures. In this case, the substrate material is in contact with a monomer solution to which the graft polymer is added. (3) Finally, the exposure to the radiation of peroxide groups on the surface, leading to the formation of a radical species (e.g., RO_2^{\cdot}) will decompose or the addition of a radical species (e.g., RO_2^{\cdot}) will decompose the peroxide groups to form free radicals that can initiate the graft polymerization. Grafts formed by energetic irradiation of the substrate are often thick (> 1 μ m), however, they are well bonded to the substrate material. Since many graftable monomers are available, wide-range surface structures can be created. Mixtures of monomers can form unique graft copolymers (Kramer and Hoffman, 1980). For example, the hydrophilic

hydrophilic ratio of surfaces can be controlled by varying the ratio of a hydrophilic and a hydrophobic monomer in the grafting mixture (Ritter and Hoffman, 1980; Ritter et al., 1979).

Photoinduced grafting (usually with visible or UV light) represents a unique subcategory of surface modifications for which there is growing interest. There are many approaches to effect this photoinduced covalent coupling. For example, a phenyl radical group can be converted to a highly reactive species upon UV exposure. This species will quickly react with any organic groups. If a substrate polymer is prepared with any organic groups and the polymer is exposed simultaneously to UV light and a substrate polymer or polymeric material, the polymer containing the phenyl radical groups will be immobilized to the substrate (Kramer and Brown, 1979). Another method involves the coupling of a bisphenol monomer to a hydrophilic polymer (Dunkley et al., 1991). In the presence of UV irradiation, the bisphenol monomer is coupled to a reactive species that can covalently couple to many polymers.

Radiation, electron, and photografting have frequently been used to bond hydrogels to the surface of hydrophobic polymers (Kramer and Brown, 1980; Dunkley et al., 1991) (see also Chapter 2.4). The protein interactions (Fahnestock and Hoffman, 1979), cell interactions (Kramer et al., 1979; Kramer and Brown, 1980), blood compatibility (Chaplin, 1983; Hoffman et al., 1982), and tissue reactions (Green et al., 1979) of hydrogel grafts surfaces have been investigated.

RGD Plasma Deposited and Other Plasma Gas Processes

RGD plasma, as used for surface modification, is a low-pressure (torr) gas environment typically at ambient (or slightly above ambient) temperatures. They are also referred to as glow discharges or gas discharge plasmas or treatments. Plasma can be used to modify existing surfaces by ablation or etching reactions or, in a deposition mode, to overcoat surfaces (Fig. 1). Good review articles on plasma deposition and its application to biomaterials are available (Yasuda and Gosteli, 1982; Hoffman, 1980; Kramer et al., 1979). Some biomaterial applications of plasma-modified biomaterials are listed in Table 3. Since we believe that RGD plasma surface modification have special promise for the development of improved biomaterials, they will be emphasized in this chapter. The specific advantages of plasma-deposited films (and to some extent, plasma-treated surfaces) for biomedical applications are:

1. They are conformal. Because of the penetrating nature of a low-pressure gas environment in which transport of mass is governed by both molecular (free) and light (diffusion) and convective diffusion, complex geometric shapes can be treated.
2. They are free of voids and pinholes. This continuous barrier structure is suggested by transport and electrical property studies (Kramer et al., 1984).
3. Plasma-deposited polymeric films can be grafted upon almost any solid substrate, including metals, ceramics,

TABLE 3. Biomedical Applications of Glow Discharge Plasma-Induced Surface Modification Processes

A. Plasma treatment (etching)	B. Plasma treatment (etching) and plasma deposition	C. Plasma treatment (etching) and plasma deposition
1. Chitosan	1. Cross-link surface molecules	1. Cross-link surface molecules
2. Sealing	2. Plasma treatment (etching) and plasma deposition	2. Plasma treatment (etching) and plasma deposition
3. Cross-link surface molecules	3. Plasma treatment (etching) and plasma deposition	3. Plasma treatment (etching) and plasma deposition
4. Plasma treatment (etching) and plasma deposition	4. Plasma treatment (etching) and plasma deposition	4. Plasma treatment (etching) and plasma deposition
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9. Plasma treatment (etching) and plasma deposition	9. Plasma treatment (etching) and plasma deposition	9. Plasma treatment (etching) and plasma deposition
10. Plasma treatment (etching) and plasma deposition	10. Plasma treatment (etching) and plasma deposition	10. Plasma treatment (etching) and plasma deposition

and semiconductors. Other surface grafting or surface modification technologies are highly dependent upon the chemical nature of the substrate.

They exhibit good adhesion to the substrate. The energetic nature of the gas phase species in the plasma treatment can facilitate ablation, implantation, penetration, and reaction between the overlayer film and the substrate.

Unique film chemistries can be produced. The chemical structure of the polymeric overlayer films produced by the plasma deposition usually cannot be synthesized by conventional organic chemical methods.

They can serve as excellent barrier films because of their pinhole-free and dense, cross-linked nature.

Plasma-deposited films generally show low levels of leachables. Owing to their highly cross-linked nature, plasma-deposited films contain negligible amounts of low-molecular-weight components that might lead to an adverse biological reaction and can also prevent leaching of low-molecular-weight material from the substrate.

These films are easily grafted. Once the apparatus is set up and optimized for a specific deposition, treatment of additional substrates is rapid and simple.

There is a mature technology for the production of these coatings. The microelectronics industry has made extensive use of inorganic plasma-deposited films (Sawada and Hail, 1983).

Although they are chemically complex, plasma surface modifications can be distinguished by infrared (IR) (Lepp et al., 1983; Haque and Baur, 1983), nuclear

magnetic resonance (NMR) (Rogers and Dill, 1981), electron spectroscopy for chemical analysis (ESCA) (Chilbert et al., 1991a), chemical derivatization studies (Gombosi and Hoffman, 1988; Gombosi and Chalkley, 1990; Chilbert et al., 1991a), and more recently scanning spectroscopy (SAMs) (Chilbert et al., 1991b, 1992).

11. Plasma-treated surfaces are useful when covered from the plasma, offering an additional advantage for cost-efficient production of medical devices.

It would be inappropriate to cite all the advantages with one also discussing some of the disadvantages of plasma deposition and treatment for surface modification. First, the chemistry produced on a surface can be ill defined. For example, if monolayers of plasma gas is introduced into the reactor, polyethylene will not be deposited on the surface. Rather, a complex, branched fluorocarbon polymer will be produced. This scrambling of monomer structure has been addressed in studies dealing with retention of monomer structure in the final film (Lopez and Ramey, 1991, 1992). Second, the apparatus used to produce plasma deposition can be expensive. A good laboratory reference will cost \$10,000-\$20,000, and a production reactor can cost \$100,000 or more. Third, a uniform reaction within long, narrow pipes can be difficult to achieve. Finally, contamination can be a problem and care must be exercised to prevent extraneous gases and pump oils from entering the reaction zone. However, the advantages of plasma reactions outweigh their potential disadvantages for many types of modifications that cannot be accomplished by any other method.

THE NATURE OF THE PLASMA ENVIRONMENT

Plasmas are ionically and molecularly dissociated gaseous environments. A plasma environment contains positive ions, negative ions, free radicals, deuterons, atoms, molecules, and photons. Typical conditions within the plasma include an electron energy of 1-10 eV, a gas temperature of 25-600°C, an electron density of 10^9 to $10^{12}/\text{cm}^3$, and an operating pressure of 0.005-1.0 torr.

A number of processes can occur on the substrate surface that lead to surface modification or deposition. First, a complex energy takes place between deposition and etching by the high-energy plasma species (Chilbert, 1992). When deposition is more rapid than etching, deposition will be observed. Because of its energetic nature, the deposition of etching processes can result in substantial chemical and morphological changes to the substrate. A number of mechanisms have been postulated for the deposition process. A reactive gaseous environment may create free radicals and other reactive species on the substrate surface that react with and polymerize molecules from the gas phase. Alternatively, reactive small molecules in the gas phase could combine to form higher molecular weight units or particulates that may settle or precipitate onto the surface. More likely the deposition observed are formed by some combination of these two processes.

PRODUCTION OF PLASMA ENVIRONMENTS FOR DEPOSITION

Many experimental variables relating both to reaction conditions and to the substrate onto which the deposition is placed affect the final outcome of the plasma deposition process (Fig. 3). A diagram of a typical laboratory setup for plasma deposition is presented in Fig. 3. The major subsystems that comprise this apparatus are a gas introduction system (control of gas mixing, flow rate, and mass of gas entering the reactor), a vacuum system (maintenance and control of reaction pressure and inhibition of backstreaming of components from the pump), an energizing system to efficiently couple energy into the gas phase within the reactor, and a reactor onto in which the samples are treated. Radio frequency, acoustic, or microwave energy can be coupled to the gas phase. Devices for monitoring the molecular weight of the gas phase species (mass spectrometers), the optical emission from the glowing plasma (spectrometers), and the deposited film thickness (ellipsometry, vibrating quartz crystal microbalance) enable one to study trends on plasma reactions.

RFED PLASMAS FOR THE IMMOBILIZATION OF MOLECULES

Plasmas have often been used to immobilize organic functional groups (e.g., amino, hydroxyl) on a surface that can be activated to attach biomolecules (see Chapter 2.11). Certain reactive gas environments can also be used to directly immobilize organic molecules such as antibodies. For example, a poly-(ethylene glycol)-poly(ethylene glycol) block copolymer substrate will adhere to polystyrene via the propylene glycol block. If the polystyrene surface with the attached substrate is briefly exposed to an argon plasma, the poly(ethylene glycol) block will be cross-linked, thereby leading to the covalent attachment of pendant poly(ethylene glycol) chains (Giles et al., 1992).

HIGH-TEMPERATURE AND HIGH-ENERGY PLASMA TREATMENTS

The plasma environments described here are of relatively low energy and low temperature. Consequently, they can be used to deposit organic layers on polymers or inorganic substrates. Under higher energy conditions, plasmas can effect surface and important functional group modifications on non-polymeric substrates. For example, fluorocarbon deposition involves exposing a high-purity, relatively slowly divided (~100 mtorr) metal powder to a high-velocity plasma of fluorine. The method is partially under patent (the surface and etching rapidly (see Chapter 2.2 for additional information).

Standardization

The proposed standardization of typical plasma surface modification reaction is illustrated in Fig. 4. Similar reactions can be

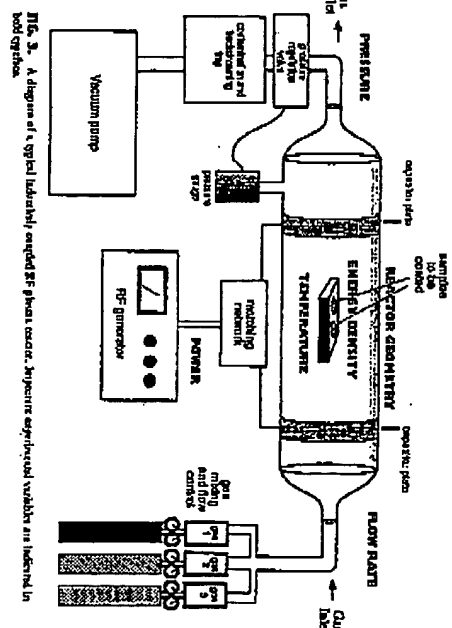


FIG. 3. A diagram of a typical laboratory setup for plasma deposition. Dependent experimental variables are indicated in bold type.

TABLE 4. Situations for Surface Modification of Biomaterials

X = leaving group	X = functional group
—Cl —OCH_3 $\text{—OCH}_2\text{CH}_3$	$\text{—CO}_2\text{R}$ —CONH_2 $\text{—CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ $\text{—CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$ $\text{—CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_2\text{CH}_3$

Gas Phase Implants

The ion beam method involves accelerated ions with energies ranging from 10^3 to 10^6 eV (1 eV = 1.6×10^{-19} joules) into the surface zone of a material to alter its surface properties. It is largely, but not exclusively, used with metals and other inorganic systems. Ions formed from most of the atoms in the periodic table can be implanted, but not all provide useful modifications of the surface properties. Important potential

used to modify hydroxylated or amine-rich surfaces. Since gases, silicon, germanium, aluminum, and quartz surfaces, as well as many metal oxide surfaces, are all rich in hydroxyl groups, silanes are particularly useful for modifying these materials. Direct evidence for surface modification on these substrates is observed by an increase in contact angle, particularly where silanes are available, permitting many different chemical functionalities to be incorporated on surfaces (Table 4). The advantages of silane reactions are their simplicity and stability, which are attributed to their covalent, cross-linked structure. However, the link between a silane and a hydroxyl group is also readily subject to basic hydrolysis, and film formation under some conditions must be considered (Wassenaar et al., 1988). Silanes can form two types of surface film structures. If only surface reactive groups (hydroxyls) are present, the silane will form a monolayer. However, if more water is present, a thicker silane layer can be formed that consists of both Si-O groups bonded to the surface and silane units participating in a "body" three-dimensional, polycondensed network. The initial steps in the formation of a thicker silane film are suggested by the reaction of the groups as in right side of Fig. 4D. A new class of three-dimensional surface films upon the former highly ordered structure has been forming considerable attention (Wassenaar et al., 1988). These self-assembled monolayers are described in more detail later in this chapter. Many general reviews on surface adhesion are available (Akhie, 1997; Finkelstein, 1980).

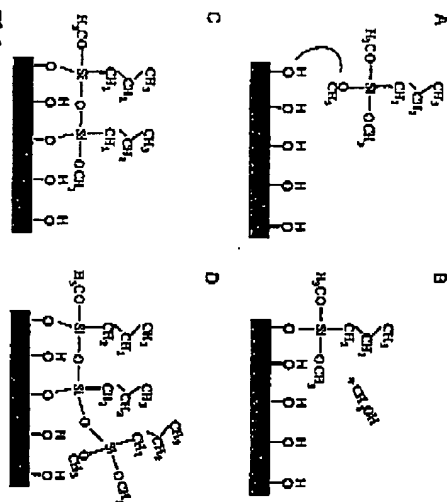


FIG. 4. The chemistry of a grafted silane surface. (A) A hydroxylated surface is treated with a silane containing a propyl (hydroxymethyl) group. (B) One of the hydroxyl groups of the propyl group is deprotected, leaving a hydrogen atom. (C) The deprotected group is removed from the surface. (D) The surface is now covered with a hydrogen atom. The molecule is held into the silicon film network, but is not directly bonded to the surface.

application for biomaterials include modification of hardness (wear), lubricity, roughness, corrosion, conductivity, and biocompatibility.

If an ion with an energy greater than a few electron volts hits a surface, the probability that it will enter the surface is high. High energy densities are also transferred to a localized surface zone over short periods. Some considerations for the ion implantation process are illustrated in Fig. 5. These surface changes must be understood quantitatively for precise engineering of new surface characteristics. Many review articles are available on ion implantation processes for tailoring surface properties (Peters and Papp, 1984; Shadmeh, 1987).

Specific examples of biomaterials that have been altered by ion implantation processes are plentiful. Titanium was ion implanted in a Ti-6Al-4V alloy to improve corrosion resistance (Bouchard et al., 1990). Implanting nitrogen into titanium greatly reduces wear (Shadmeh, 1987). The ion implantation of boron and carbon into type 316L stainless steel improves the high-cycle fatigue life of these alloys (Gibson et al., 1987).

Langmuir-Blodgett Deposition

The Langmuir-Blodgett (LB) deposition method covers a surface with a highly ordered layer. Each of the molecules

that assemble into this layer contains a polar head group and a nonpolar region. The deposition of an LB film using an LB trough is illustrated schematically in Fig. 6. By pulling the vertical plate through the air-water interface, and then pushing the plate down through the interface, leaving the surface film on the air-water interface, compressed as all forces (as illustrated in Fig. 6), multilayer structures can be created. Some components that form organized LB layers are shown in Fig. 7. The advantages of films deposited on surfaces by this method are their high degree of order and uniformity. Also, since a wide range of chemical structures can form LB films, there are many options for incorporating new chemicals at surfaces. The stability of LB films can be improved by crosslinking or polymerizing the molecules together after film formation, often through double bonds in each molecule (Miller et al., 1988). A number of research groups have investigated LB films for biomedical applications (Raymond and Chapman, 1984; Bird et al., 1985; Chiu et al., 1990). Many practical systems on these surface structures are available (Kinsch, 1990; Uman, 1991).

Self-Assembled Monolayers

Self-assembled monolayers (SAMs) are surface-coating films that spontaneously form as highly ordered structures (two-

dimensional) crystals on specific substrates (Paine et al., 1988; Uman, 1991; Whiteside et al., 1991). In some ways SAMs resemble LB films, but there are important differences. Examples of SAMs films include *n-octyl* chains on hydroxylated surfaces (Silber, 1988), alkanes, silanes, siloxanes, and alcohols on some metals (gold, silver, copper), oxides and silicon on silicon, and carboxylic acids on aluminum oxide and silver. Most molecules that form SAMs have the general characteristics illustrated in Fig. 8.

Two processes are particularly important for the formation of SAMs (Uman, 1991): a strong, covalent adsorption of an anchoring chemical group to the surface (typically 30–100 kcal/mol), and van der Waals interaction of the alkyl chains. The strong bonding to the substrate (chemisorption) provides a driving force to fill every site on the surface and to displace contaminants from the surface. This process is analogous to the compression of the LB film by the movable barrier in the trough. Once every adsorption site is filled to the surface, the chains will be in sufficiently close proximity to each other so that the van der Waals interaction forces between chains can exert their influence and lead to a crystallization of the alkyl groups. Molecule mobility is an important consideration in this coating formation process so that (1) the molecules have sufficient time to migrate into position for a tight packing of the chains and groups at the surface and (2) the chains can enter the surface. The advantages of SAMs are their ease of formation, the chemical stability (often considerably higher than comparable LB films), and the many options for designing the functional

group that interfaces with the world. Although the discovery of SAMs is relatively recent, biomaterials applications have already been suggested (Kawakami et al., 1989; Paine and Whiteside, 1991).

Surface-Modifying Additives

Certain components can be added in low concentrations to a material during fabrication and will spontaneously migrate to and dominate the surface (Ward, 1989). These surface-modifying additives (SMA)s are well known for both organic and inorganic systems. The driving force to concentrate the SMA to the surface after leaving the SMA with a biomaterial to be surface modified (the bulk material) is entropic—the SMA should reduce the interfacial energy. To do this, two factors must be taken into consideration. First, the magnitude of the difference in interfacial energy between the system with and without the additive and the same system with the SMA at the surface will determine the strength of the driving force leading to a SMA-dominated surface. Second, the mobility of the bulk material and the SMA additive molecules within the bulk will determine the rate at which the SMA reaches the surface, or if it will get there at all. An additional concern is the durability and stability of the SMA at the surface.

A typical SMA designed to alter the surface properties of a polymeric material will be a relatively low-molecular-weight alkylsiloxane copolymer (see Chapter 2.3). The "A" block will be capable of, or comparable with, the bulk material; this

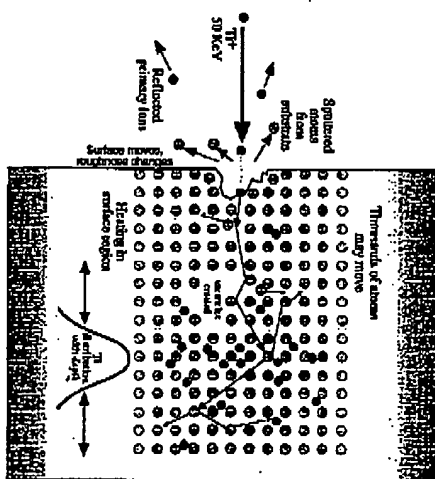


FIG. 5. Some considerations for the high modulus process.

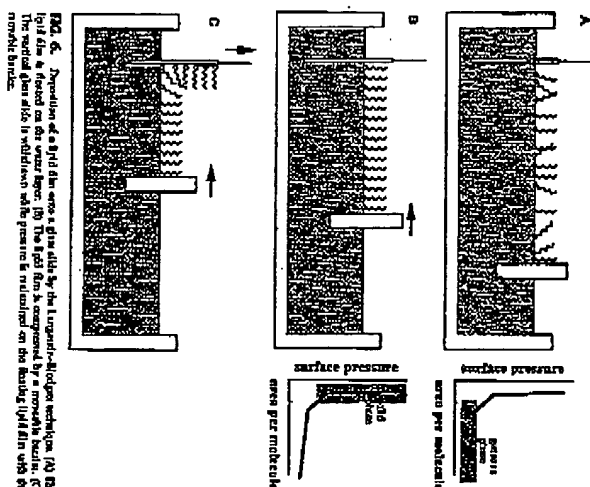


FIG. 6. Deposition of a hybrid film. (A) The film is formed on the substrate. (B) The film is composed of a porous layer. (C) The porous layer is infiltrated with the polymer. (D) The film is cured.

which the SMA is being added. The "A" block will be incompatible with the bulk material and have lower surface energy. Thus, the A block will anchor the B block and the material to be modified at the interface. This is suggested schematically in Fig. 9. During initial fabrication, the SMA might be distributed uniformly throughout the bulk. After a period for curing or an annealing step, the SMA will migrate to the surface.

For example, an SMA for a polyurethane might have a low-molecular-weight polyurethane A block and a polydimethylsiloxane (PDMS) B block. The A block will anchor the SMA in the polyurethane bulk, the polyurethane A block should be reasonably compatible with the bulk polyurethane, while the low-surface-energy, highly flexible, siloxane B block will be exposed at the air surface to lower the interfacial energy (note that air is "hydrophobic"). The A block anchor should confer stability to the system. However, if the system is placed in an aqueous environment, a low-surface-energy (in air) polymer (the B block) is now in contact with water—a high interfacial energy situation. If the system,

after fabrication, still exhibits sufficient chain mobility, it might phase invert to bring the bulk polyurethane on the A block to the surface. Unless the system is specifically engineered to do such a surface phase reversal, this inversion is undesirable. Proper choice of the bulk polymer and the A block can impart surface phase inversion.

Many SMAs for inorganic systems are known. For example, very small quantities of noble will completely alter the structure of a silicon (11) surface (Pfeiffer and Ching, 1987). Copper will segregate to the surface of gold alloy (Kronka et al., 1988). Also, in molten steel, chromium will concentrate (at the oxide) in the surface, imparting corrosion resistance.

There are a number of additives that spontaneously surface concentrate, but are not necessarily designed as SMAs. A few examples for polymers include PDMS, some extrusion stabilizers (Harris, 1983), and some UV stabilizers (Yip et al., 1992). The presence of such additives at the surface of a polymer may be unexpected and they will not necessarily form stably, durable surface layers.

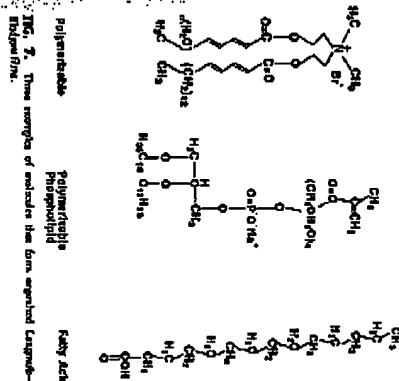


FIG. 7. Three examples of molecules that form organized Langmuir-Blodgett films.

Conversion Coatings

Conversion coatings modify the surface of a metal, like a dense oxide-rich layer that imparts corrosion protection, enhanced adhesion, and sometimes lubricity to the metal. Such is frequently accomplished (reacted with phosphoric acid) or etched (with chromic acid). Aluminum is electrochemically

Plasma Coating

Teflon (polytetrafluoroethylene) coatings occupy a unique niche in the surface modification literature because of their frequent application and the good quality of the thin film coatings formed (Lub et al., 1977; Nakabe et al., 1984). The deposition method is also unique and involves the formation of a

modified inductive, overall, or surface field (photoresist). Another method may also be used for surface-modifying stainless steel and Ti-Al alloys (Fineman, 1990; Kierma and Lamm, 1983).

The conversion of metallic surfaces to "oxide-like" electrochemically passive states is a common practice for base-metal alloy systems used as biomaterials. Standard and recommended techniques have been published (e.g., ASTM F46) and are relevant for most nonoxidized base-bearing surgical implants. The hydrophobic literature regarding these types of surface passivation techniques has been summarized (Neh

Raman, 1986). Base-metal alloy systems, in general, are subject to electrochemical corrosion ($M \rightarrow M^+ + e^-$) within active corrosion elements. The rate of this corrosion process is reduced 10-100 times by the presence of a relatively conductive, relatively inert oxide surface. For many metallic devices, exposure to a neutral salt (e.g., sulfuric acid in water) for up to 30 min will provide a passivated surface (i.e., protected by its own oxide).

The reason that many of these surface modifications are called "oxide-like" is that the structure is complex, including OH, H, and anions that may or may not be crystalline. Since most passive surfaces are thin films (50-5000 $\times 10^{-6}$ cm), and are transparent or metallic in color, the surface appears similar before and after passivation. Further details on surfaces of this type can be found in Chapters 12, 23, and 63.

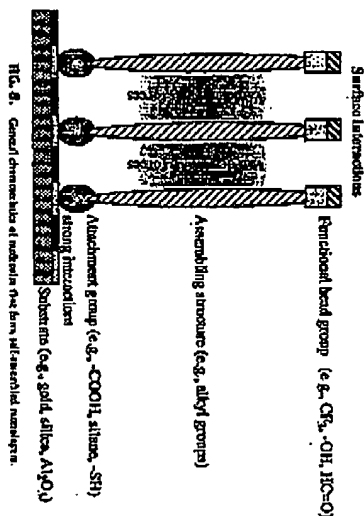


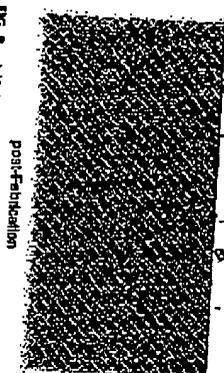
FIG. 8. General description of molecules in the form of self-assembled monolayers.



Publication Information

and PVA monomer is reported at 175°C and 1 ton, pyrolysis at 700°C and 0.5 ton, and finally dependent on a substrate at 25°C and 0.1 ton. The coating has excellent abrasion resistance and moisture barrier properties, and has been used to protect implanted electronics (Lorb et al., 1977b). Nichols et al. (1964) used electronic circuitry (Spilvack and Ferrara, 1969).

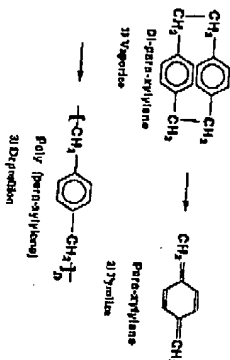
Laser Method



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oxation, pyrolysis, degradation, and polymerization of the monomers, di-para-xylylene (DPX), according to the following reaction:



The blood compatibility of these devices is being actively explored to enhance aspects of performance. Since a given medical device may at times be used in a variety of ways, it is important that the device be able to readily have appropriate performance characteristics, physical properties, and chemical biocompatibility, without the need for redesign, modification, or replacement of the device without the need for redesign, according for manufacturing, and determining of medical personnel.

CONCLUSIONS

The blood compatibility of these devices is being actively explored to enhance aspects of performance. Since a given medical device may at times be used in a variety of ways, it is important that the device be able to readily have appropriate performance characteristics, physical properties, and chemical biocompatibility, without the need for redesigning or modification of the device without the need for redesign, according for manufacturing, and determining of medical personnel.

Acknowledgments

in honor of the late Professor J. Lemons have increased this chapter and are appreciated.

पुष्पकान्त

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2.10 FABRICS

Shalaby W. Shalaby

The use of fabrics and other fibrous forms as biomaterials dates back to the early Egyptians and Indians. Linen sutures and strips was used by the Egyptians with natural adhesives to draw the edges of wounds together to achieve proper healing and retention of original strength. The American Indians used horsehair, cotton, and thin leather strips (Shalaby, 1985) for a similar purpose. More recent use of fabrics as biomaterials was generally viewed as an extended application of the traditional woven and knitted forms of textiles. Prior to the development of the polyethylene terephthalate-based vascular grafts (Hoffman, 1977; Williams and Roaf, 1973), woven, nonwoven and knitted cellulosic fabrics represented the major types of fibrous materials used by the health care industry. Over the past few decades, with the development of sophisticated polymer and fiber processing technologies, nontraditional forms of fabrics, and fabriclike fibrous products have become available and used successfully as biomaterials in old and new applications (Boretos and Edeen, 1984). Hence, it is an objective of this chapter to survey the major traditional and nontraditional forms of fabric constructions and related products and provide brief descriptions of the constituent materials, their processing and properties. A list of physical and biological characterization and test methods is also provided.

TYPES OF FABRICS AND THEIR CONSTRUCTION

Textile fabrics of woven, nonwoven, and knitted types have been used in one or more biomedical applications. These fabrics are made from a wide range of natural and synthetic fibers, as described in fiber and textile science publications (Joseph, 1981, 1984; Labarthe, 1975; Moncrieff, 1975). Descriptions of these fibers and their parent polymers are given in Tables 1-A to 1-C. The processing and characterization of fabrics are addressed in detail in these publications. In a review of fibrous materials for biomedical applications by Shalaby (1985), major types of materials were highlighted. The formation and characterization of unconventional constructions (some of which are not assembled by fiber processing), such as expanded porous poly(tetrafluoroethylene) (Gore-Tex, W. L. Gore and Assoc., Inc.) and hollow fibers, are discussed in a few reviews (Collier, 1970; Hoffman, 1977; Shalaby, 1985; Shalaby *et al.*, 1984). The characterization and testing of fibrous devices and fabric surfaces have been reported in a few reviews (Cooper and Peppas, 1982; Hoffman, 1977; Hastings and Williams, 1980). Important aspects of these constructions are outlined in Table 2.

Cellulose fibers from cotton or wood pulp are the natural fibers most commonly used in the production of biomedical fabrics and related construction. Highly absorbent cellulose fibers, obtained in recent years by fermentation, may find use in certain sanitary products such as napkins. The small production of these fibers, however, may limit their application. Although cellulose acetate and viscose rayon are less commonly used as fibers than cellulose, interest in other regenerated natu-

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